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Spin polarized photoemission studies of the Gd(0001) surface[1]

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Abstract

The surface magnetic properties of the rare earth Lanthanide, gadolinium (Gd) have been the subject of a number of different experimental and theoretical studies in recent years. These studies have suggested that the surface of Gd exhibits a variety of unusual magnetic properties including imperfect ferromagnetic coupling between the surface and bulk, canted magnetic moments and some form of phase transition. Also the temperature dependent behavior appears to be quite controversial with both a Stoner-like and spin-mixing behavior invoked to describe the loss of magnetization. With new angle- and spin-resolved studies carried out at room and low temperatures, we re-examine this temperature dependence and confirm that both types of behavior are evident. We further provide direct evidence that at the temperature of liquid nitrogen, it is possible to observe a canting of the surface moments out of the surface plane. © 1998 Published by Elsevier Science B.V. All rights reserved

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1. Introduction

The surface magnetic properties of the rare earth Lanthanide, gadolinium (Gd), have been the subject of a number of different experimental and theoretical studies in recent years. The ferromagnetism of bulk Gd with a Curie temperature $T_c^b = 293$ K reflects the coupling of localized 4f shell moments via an RKKY type interaction involving the more itinerant 5d electrons. Surface studies employing electron capture spectroscopy suggested that the Gd surface layer exhibits a Curie temperature some 20 K higher than that of the bulk [1]; an observation that was later confirmed by spin polarized low-energy electron diffraction studies combined with magneto-optic Kerr effect (MOKE) measurements [2]. Using spin polarized core level photoemissions, the authors of the latter study also concluded that the surface magnetic moments were antiferromagnetically coupled to the bulk. An antiferromagnetic alignment of surface and bulk moments was supported by a theoretical study employing the full-potential linearized augmented-plane wave (FLAPW) method [3].

Photoemission studies of the clean Gd(0001) surface lead to the identification of a surface state of d_{z^2} symmetry sitting immediately below the Fermi level [4]. Subsequent photoemission studies of the spin polarization in this state provided clear evidence, contrary to the earlier conclusions, that the surface is in fact ferromagnetically aligned with the bulk [5]. More recent theoretical studies support this observation and suggest that the incorrect conclusion of the earlier theoretical study probably reflected an inadequate treatment of correlation energies in the LSDA approach [6,7].

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Studies of the secondary electron emission show a significant perpendicular, as well as in-plane component of spin polarization [8]. This perpendicular component was observed to persist to temperatures well above the bulk Curie temperature, an observation that was interpreted as an indication of canted moments in the surface region. Observations of the surface and bulk contributions to the spin polarization in the Gd 4f levels have led to the same conclusion [9,10].

There have also been a number of studies of the temperature dependence of the surface magnetization. A spin polarized photoemission study of the surface state, at temperatures close to the Curie temperature, concluded that the binding energy of the surface state was essentially fixed and that the magnetization was lost via a spin-mixing process [11]. This conclusion was challenged in two subsequent papers. A high resolution photoemission study of the occupied surface state found that with increasing temperature, the state moved closer to the Fermi level [12]. A spin polarized inverse photoemission study of the unoccupied minority spin counterpart found that this state also moved towards Fermi level as the temperature increased [13]. Thus, both of the latter studies concluded that the surface state displays a Stoner-like behavior, similar to that observed in a photoemission study of the temperature dependence of the bulk 5d band [14]. The latter reduction in the exchange splitting observed for the Gd conduction bands was reproduced in a theoretical calculation by Nolting, et al. [15] who found a ‘‘Stoner-like’’ temperature dependence for the weakly correlated ‘‘s-like’’ dispersions, but a different behavior for the more strongly correlated ‘‘d-like’’ dispersions.

In this paper we again examine the temperature dependence of the binding energies and spin polarization of the Gd surface state. Furthermore, using a new instrument we are able to directly search for an out of plane component of the spin polarization. This represents the first time that such a search has been restricted specifically to the surface region. The earlier secondary electron study was at such an energy that there would be no specific surface sensitivity. Within the limits of detection, no out of plane component is observed at room temperature. However, an out of plane component is observed at liquid nitrogen temperature. The measured polarizations indicate that the surface moments are canted approximately 6° out of the surface plane.

2. Experimental

The experimental studies reported in this paper were carried out on a new facility based on the use of a Scienta SES200 analyzer [16]. This instrument may be operated in two modes allowing either a high resolution angle resolved photoemission capability or a spin resolved photoemission capability. In the former case the output of a two dimensional detector is monitored with a CCD camera, the output of which is coupled to a frame grabber. In the present system rather than a rapid cycling of the frame grabber, the camera has been modified to allow much of the signal integration to be carried out within the camera itself.

In the spin polarized mode the two-dimensional detector and CCD camera are removed and replaced by a new spin polarimeter of the micro-Mott variety. Described in greater detail elsewhere [17], the spin polarimeter represents a modification to the designs developed by the Rice University Group [18]. In the present design, the use of electron optics allows a larger solid angle of scattered electrons to be collected. This, in turn, leads to an improved figure of merit. Shown in Fig. 1, the spin polarimeter operating at a scattering energy of 25 keV is coupled to the Scienta analyzer with electron optics which include a simple plane mirror deflector. This deflection allows the measurement of two orthogonal components of spin. Thus, magnetizing a thin film sample along an axis running up through the center of the chamber, the two components would reflect the in-plane and perpendicular magnetization.

Gadolinium films were prepared by evaporation onto a Mo(110) substrate. Following standard procedures, the evaporated films of thickness 200 A were annealed at 750 K for 1 min to produce relatively well-defined surfaces. Low energy electron diffraction (LEED) was used to monitor crystallographic order in the films. The presence of any contaminants such as oxygen were monitored within the photoemission spectra. UV photons for the study described in this paper were provided by a resonance lamp. The energy resolution in both the angle-resolved and spin-resolved studies reported here is of the order of 50 meV. The angular resolution in the angle-resolved studies is of the order of 0.2°.

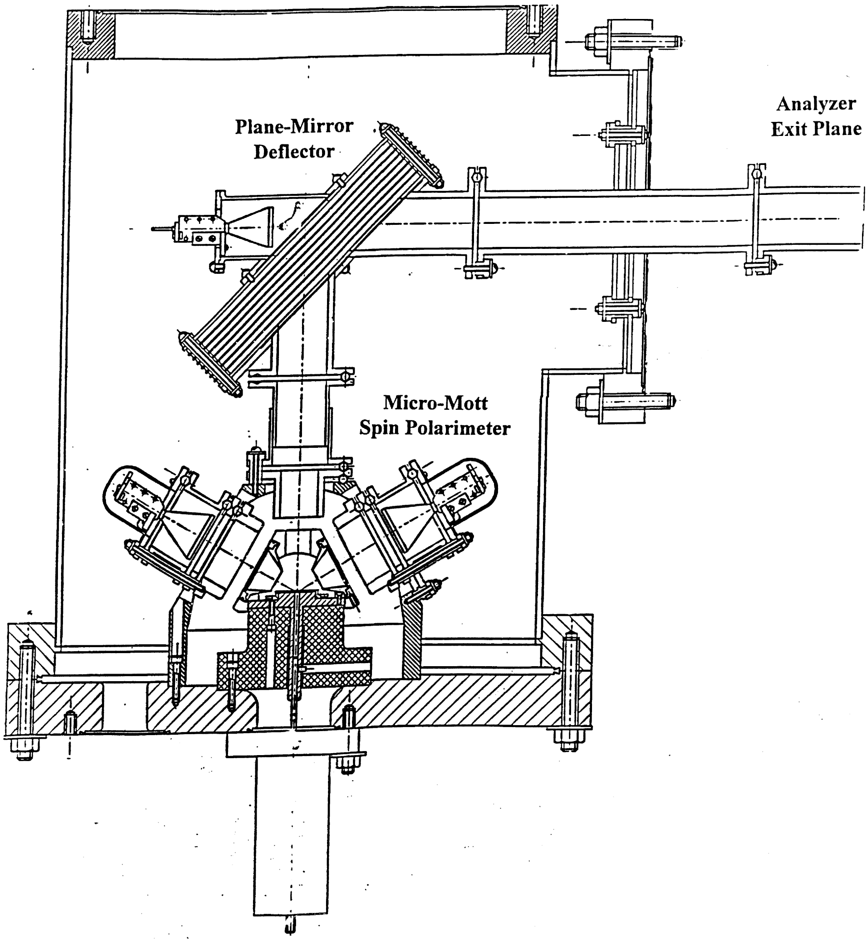

Fig. 1. The electron optics and spin polarimeter that are coupled to the Scienta SES200 analyzer. The use of a plane mirror deflector allows two components of the spin to be measured simultaneously.

3. Results

In Fig. 2 we show a spectral density map recorded in the $\bar{\Gamma}\bar{M}$ azimuth from the clean Gd(0001) surface at two different temperatures. An immediate observation is that phonon broadening results in a considerable increase in the width of the surface state as the temperature is increased from 82 to 300 K. A similar broadening has also been reported elsewhere. Phonon broadening in photoemission spectra has been the subject of a number of studies in recent years [19,20]. At temperatures above the Debye temperature, the width of a photoemission peak has been shown to increase linearly with temperature. In this high temperature limit the change in width Δw is related to the change in temperature ΔT by the expression $\Delta w = 2\pi\lambda k\Delta T$ where λ represents the electron–phonon coupling constant.

Examination of Fig. 2 shows that in the lower temperature plot the surface state retains an approximately constant width until the angle of emission exceeds 5°. From comparisons with calculated bandstructures [3], it is clear that at this point the state is leaving the bulk band gap and beginning to resonate with the bulk bands. This leads to a considerable reduction in the lifetime of any photohole and the band broadens accordingly. The resonance will of course be with bulk bands of the same spin.

As the temperature is raised to room temperature the entire surface band shifts to a lower binding

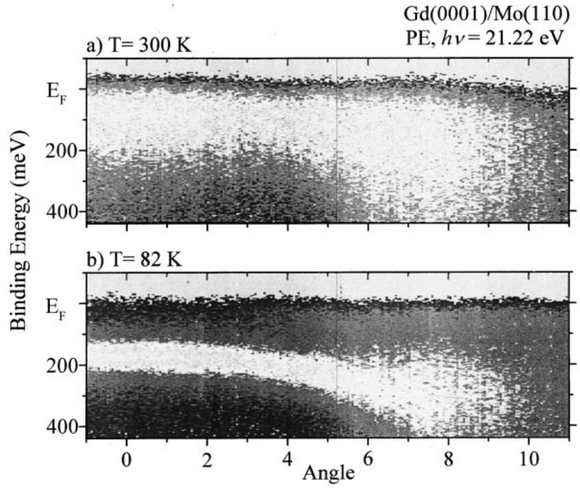

Fig. 2. Spectral density plot obtained in the $\bar{\Gamma}\bar{M}$ azimuth from the clean Gd(0001) surface, as a function of temperature. The lower plot shows the emission at a temperature of 82 K and the upper plot the emission at a temperature of 300 K. The photon energy in these studies was 21.2 eV.

energy close to the Fermi level. This is highlighted in Fig. 3 where we show cuts through the spectral density map of Fig. 2 at three different angles. In fact, the shift in energy as a function of temperature is of a similar magnitude across the entire band.

In Fig. 4 we show angle-integrated spin resolved spectra recorded from the clean Gd surface at a

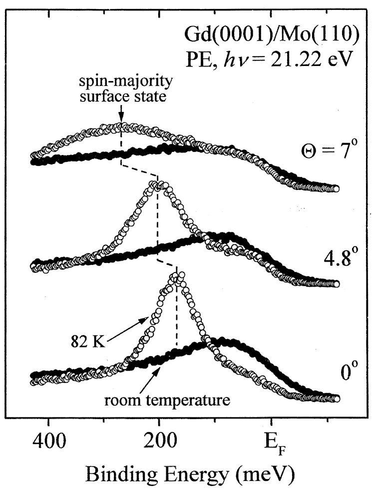

Fig. 3. Photoemission spectra as a function of angle extracted from the data shown in Fig. 2. The spectra are shown for the two different temperatures. The incident photon energy is again 21.2 eV.

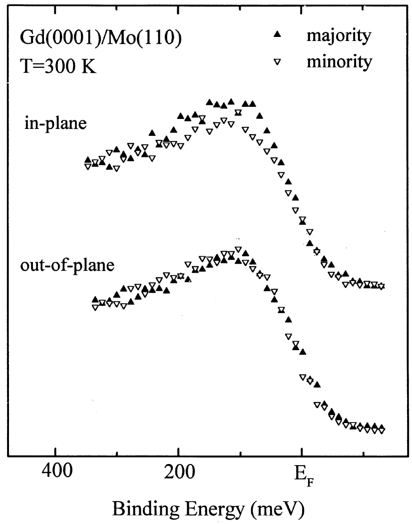

Fig. 4. Spin polarized photoemission spectra recorded from the clean Gd(0001) surface at 300 K. The upper spectra reflect the polarization in-plane, the lower spectra represent the polarization out of plane. As indicated the majority spin are represented by the filled triangles, the minority spin by the empty triangles.

temperature of 300 K. Both the in-plane and perpendicular components are plotted. The figure clearly shows a spin polarization of approximately 5% for the in-plane component but no measurable polarization for the perpendicular component. In that there appears no splitting between the two spin components, the polarization measurement for the in-plane component is in good agreement with the measurements reported elsewhere by Li et al. [11]. However the lack of any measurable polarization in the perpendicular component is in contrast to any models suggesting that the residual perpendicular polarization observed in secondary electron studies is due to a strong surface contribution.

Fig. 5 shows angle-integrated spin-resolved spectra recorded from the clean Gd surface at a temperature of 80 K. Using Fig. 3 it is clear that at this temperature, even though the spectra in Fig. 5 are angle-integrated, the majority of the emission comes from the region of low dispersion close to the surface normal. Fig. 3 again shows the in-plane and perpendicular components. Firstly examining the in-plane component, we note that both the majority and minority spin components are well displaced from the Fermi level. The source of the minority component is unclear. It may reflect incomplete saturation the film

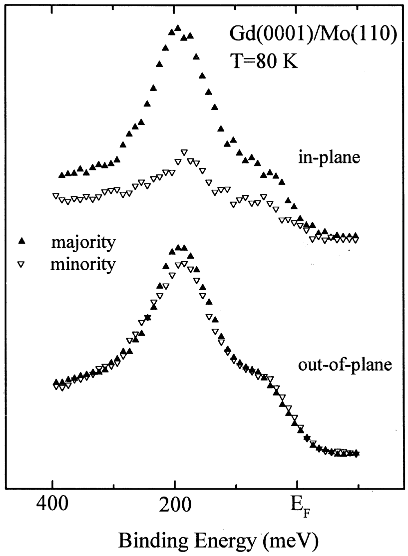

Fig. 5. Spin polarized photoemission spectra recorded from the clean Gd(0001) surface at a temperature of 80 K. The upper spectra reflect the polarization in-plane, the lower spectra represent the polarization out of plane. As indicated the majority spin are represented by the filled triangles, the minority spin by the empty triangles.

or it may reflect some form of spin-mixing. In the latter case the emission or adsorption of a magnon with spin one would result in the spin re-orientation from one spin component to the other. Obeying Boson statistics, the latter effect would manifest itself in the spectra down to very low temperatures as has been observed in studies of bulk Gadolinium. Nolting et al. [15] have in fact discussed such behavior. However in their study the effect was not obviously accompanied by the shift in binding energies observed in the present study.

More interestingly however, we note that at this temperature a small perpendicular component is observed in the spin polarization. This observation provides evidence of a canting of the surface moment. Further from the measured perpendicular and in-plane polarizations we conclude that the moments are canted to an angle of approximately 6° with respect to the surface plane.

4. Discussion

The data presented in this paper provides clear evidence supporting the earlier observations [12,13] of a ''Stoner-like'' temperature dependence of the surface state binding energy. It is important to remember that whilst ''Stoner-like'' behavior may be viewed as an indication of the way that long-range order is lost in the surface region it may also reflect the loss of long range order in the bulk. The binding energy of a surface state is determined by the boundary conditions in the surface region. The surface state examined in the present study falls within a bandgap in the 5d manifold of states. Earlier studies have examined the temperature dependence of the 5d bulk bands [13,14]. In all cases, a Stoner like behavior was observed but the shift in the binding energy of the bottom of the gap was greater than the shift observed for the top of the gap. This disparity means that the surface state will experience *temperature dependent boundary conditions*. It is also clear that the spectra shown in Figs 3 and 4 appear to exhibit spin polarization behavior, characteristic of the ''spin-mixing'' model [11]. Whether or not the latter behavior represents a topological or structural effect in that the magnetization is not completely saturated due to the presence of domains or whether the observed spin polarizations reflect the presence of magnon interactions requires further detailed study.

An important observation in the present study however, is that at low temperatures, it is possible to observe a canting of the surface moments. Such a canting of the surface moments might be anticipated on the basis of magnetic anisotropies in the surface region. Indeed studies have shown that the direction of easy magnetization shows a marked temperature dependence in the bulk [21]. Those studies indicate that the magnetic moments are canted over with respect to the c-axis, the angle of canting ranging from 0 to 65°, with the maximum canting being observed at a temperature of 180 K. The canting reflects the magnetic anisotropy within the bulk. Studies of the thickness dependence of the magnetization of Gd thin films find that the competition between the magnetostatic energy, which tends to align the moments within the film and the direction of easy magnetization, which favors out of plane alignment, leads to a thickness dependent magnetic re-orientation transition temperature [22]. In the surface region LEED studies indicate that at room temperature certainly, the surface layer is relaxed inwardly by 3.5% with respect to the bulk interlayer spacing [23]. We hypothesize that such a relaxation will lead to magnetic anisotropies in the surface region, which in turn result in the canting of the surface moments. Finally we note that we have observed the out of plane polarization at low temperature. We cannot rule out that the same canting exists at room temperature. However with such a small cant angle the polarization in the perpendicular direction would be so small as to be effectively unobservable.

Acknowledgements

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